Synopsis of the Proposed Ph.D. Research Work

Title of the Proposed Thesis:

Spectroscopic and DFT studies of Donor acceptor Organic molecules and Inorganic solids

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Origin of the Research Problem:

Spectroscopy is a technique which has wide applications in almost all branches of science. Spectroscopic techniques employ light to interact with matter and thus probe certain features of a sample. Light is electromagnetic radiation, a phenomenon exhibiting different energies, and depending on that energy, different molecular features can be probed. Infrared, ultraviolet and visible light spectroscopic techniques are commonly use to probe the molecule, molecular clusters or even extended structures. The former deals with vibrational feature of the molecule and the latter probe the electronic transition. The electronic transitions in molecules can be classified according to the participating molecular orbitals. From the four possible transitions ($n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, $n \rightarrow \sigma^*$, $\sigma \rightarrow \sigma^*$), only two can be elicited with light from the UV/Vis spectrum for some organic molecules: $n \rightarrow \pi^*$and $\pi \rightarrow \pi^*$. The $n \rightarrow \sigma^*$and $\sigma \rightarrow \sigma^*$transitions are energetically not within the range of UV/Vis spectroscopy and require higher energies.

When an organic molecule with chromophoric system involves in donor acceptor interaction it is expected to exhibit a change in chromophoric absorption. Such changes are obviously related to the reorganization or restructuring of orbital combination. Recently advancement in theoretical techniques particularly density functional theory (DFT) calculation paves a great way to understand such electronic transition as well as the vibrational features of the molecular systems. Consequently the present day chemistry, which not only consists of laboratory experimental works but it greatly depends on the theories too. And the theoretical chemists play a great role in the development of the research works. In addition, a combined experimental and theoretical calculation provides an excellent opportunity to shade light on the system under investigation.

At present we are investing a donor-acceptor organic molecular system, namely benzthiazoline-2-thione (BTT) which is responsive to UV-VIS spectroscopy. An important observation reported over half a century ago, the curious shift in UV-VIS spectra of BTT. It has been reported that the hypsochromic shift in electronic transition takes place when the chromophore is involved in hydrogen bonding as acceptor (i.e. >C=S…H—O—) and the bathochromic shift occurs when serving as donor (—N—H…O=C<) [10]. However, when BTT acts as both the donor and acceptor e.g. dimerized self-associated from in CCl_4 solvent no shift is observed. The latter observation indicates the complementing nature of blue and red shifts.[1, 2]

A number of quantum chemical investigation in terms of DFT calculations provide plenty of informations about the geometrical parameters, kinetic, tautomerism, dimerization, conformational preference, chemical hardness, energy gap between the frontier molecular orbitals, vibrational spectra, probable electronic transitions and chemical shifts for BTT and its derivatives. However, so far no attention has been paid to rationalize the observed UV spectral shift in terms of theoretical framework and the rational explanation of the observed transitions. [3-10]

Objective of the work:

The benzthiazoline-2-thione (BTT) and its derivatives are industrially and biologically important thiazole ring containing heterocyclic organic compounds. Though these compounds have been investigated over six decades, it is far from complete understanding and the results are rather controversial. About half a century ago it has been reported that the BTT can serve as a hydrogen bond acceptor and donor in different solvent resulting, respectively, hypsochromic and bathochromic shifts in chromophoric absorption. Interestingly, when the molecule itself acts as a donor and acceptor of hydrogen bond in dimeric form, no shift in the spectra is detected. Unfortunately the assignment of spectral transition of these curious observations is poor and the complexity in spectral analysis was attributed to the mixture of charge transfer transition with nominal chromophoric transitions.[1, 11]

A large number of theoretical and experimental investigations have been carried out on benzthiazoline-2-thione (BTT) and its derivatives. The BTT keto form can also exist in tautomeric enol form i.e. 2-mercaptobenzothiazole (MBT). A majority of studies have been focused on structural and vibrational spectra as well as on keto-enol equilibrium.[1, 12-17] However, the reported results are not unambiguous. Accordingly, the investigation on structural properties of BTT and its derivatives received significant interest over half a century. [18, 19]

Most of the reports suggest the prevalence of keto form. A recent report based on variable temperature proton NMR studies claim the unique existence of the BTT-keto form. Infrared and Raman spectral analysis suggest the presence of only BTT form. [20, 21] Similar conclusion was drawn from investigation on compound where ring sulfur was replaced with oxygen. [22] However, MBT is reported to have pKa of 6.93 at room temperature and confirmed to adopt either the thione or the thiol structure. [5-8] In basic medium enol form can exist in ionic state and even oxidize to

dithiolate.[5,8,9] The keto-enol form is sensitive to pH. Keto form is predominate at pH <4 and enol form dominates for pH >9. For 4 < pH < 9 both the form coexist.[8] The restricted Hartree–Fock and Becke'sthree parameter exchange correlation functional of Lee-Yang-Parr (B3LYP) with 6-31G (d,p) basis set computation suggest a favourable keto/enol (BTT/MBT) tautomerism.[19-20] On the other hand, B3P86/6-31G* and AM1 calculations supports only keto conformer.[12,14] Thus the existing reports suggest that the system is far from complete understanding. Thus the present objective is to understand the observed spectral changes in BTT system in different solvents.

Further focus will be given to perform different spectroscopic experiments like IR, UV-VIS etc. on selective donor acceptor organic molecule and to understand the observed spectral features from the theoretical point of view using DFT calculations. Emphasis will be given to locate the electronic transition, origin of spectral shift, ground and excited state charge distribution, whether any charge transfer type transition is coupled with the normal electronic excitation, possible transition state (if exist) for the donor-acceptor formation. For the case of inorganic oxides exhibiting luminescence property band structure calculation will be performed to rationalize the optical behavior of different class of oxides.

Methodologies:

The following methodologies will be adopted to carry out the proposed research work.

UU-VIS spectroscopic study:

Theoretical studies often need to be correlated with experimental observations. UV-Vis spectroscopic studies reveal the formation of a charge transfer complex and/or absorption bands which very often tend to support the theoretical results as well as helps modifying the theoretical models/ methods.

To know whether a charge transfer complex is formed or not with the help of absorption spectroscopy the spectrum which exhibits the characteristic absorption band attributed to the charge transfer transition and this band arises due to the transition of an electron from the highest occupied molecular orbital of the donor (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the acceptor. Charge-transfer related parameter as like ionization potential of the donor[23], resonance energy [24], free energy [25], oscillator strength [26], and transition dipole moment[27] etc., to be calculated.

Fluorescence spectroscopic study:

Detailed emission study of the donor-acceptor systems and their interpretation and calculation of excited state binding constant by Stern-Volmer equation. A variety of processes can result in such decreasing in intensity involving collisional or dynamical quenching, static quenching, FRET, etc. In Static Quenching fluorophores form a reversible complex with the quencher molecule in the ground state. Dynamic quencher occurs in association with a collision between fluorophore in its excited state and quencher molecule. The fluorophore returns to ground state without emission of light. On the other, in static quenching, a non-fluorescent complex is formed between the fluorophore and the quencher. Usually, only a fluorophore which is not complexes can exhibit fluorescence. The fluorophore can form a stable complex with another molecule. If this ground-state is non-fluorescent, then we say that the fluorophore has been statically quenched. In such a case, the dependence of the fluorescence as a function of the quencher concentration follows the relation called Stern-Volmer equation. FRET results in a decrease of the fluorescence intensity and lifetime of the donor probe; it enhances the fluorescence of the acceptor probe when the acceptor is fluorescent. When the donor molecule absorbs a photon, and there is an acceptor molecule close to the donor molecule, radiation lessenergy transfer can occur from the donor to the acceptor.

FT-IR study:

FTIR spectra determine structural information about a molecule. Apart from theoretical suggestions, experimental proofs are needed to check the final outcome. Calculation of transition states (TS), tautomerisation, intrinsic reaction coordination (IRC) are to be verified experimentally with FT-IR study.

XRD study:

Single crystal or powder X-ray diffraction to be very useful and has provided vital information about the actual complex composition, dimension of the unit cell, purity of the sample.

Computational strategies:

Structure optimization of the reactants, products and calculation of IRC, TS, excited states, force constants, oscillator strengths, HOMO-LUMO diagram, band structure etc. are to be calculated by theoretical studies.

With suitable methods and basis sets, the above electronic structure propertiescan be calculated using ORCA, Gaussian, Avogadro, Gaussview, Gabedit software packages[28-31]

Future Prospect

As mentioned in the preceding section, at present we are focusing on the spectroscopic experiments and its theoretical understanding using DFT calculation of donor-acceptor organic molecules in different solvents. In future we will concentrate on the similar types of system which exhibit UV sensitivity on donor-acceptor type interaction and to find the rational way of using DFT formalism to understand thephenomena.

Recently, it has been observed that several inorganic oxides in their nanodimension exhibit luminescence properties, which are dependent on structure type of the oxides. However, there is no proper understanding on such observation. It has been speculated that there are possible mid-gap energy states lying between the valence and conduction bands of these very insulating and/or semiconducting oxides. We will put emphasis tofind the physical origin of such luminescence in these inorganic oxides. Emphasis will also be given to elucidate the mechanistic path of the catalytic degradation of organic photosensitized dye catalyzed by inorganic oxide nanoparticles.

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